Dataset Paper

Heats of Solution of Liquid Solutes in Various Solvents

Vladimir D. Kiselev, Ilzida I. Shakirova, Lubov N. Potapova, Helen A. Kashaeva, and Dmitry A. Kornilov

Department of Physical Chemistry, Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya Street 18, Kazan 420008, Russia

Correspondence should be addressed to Vladimir D. Kiselev; vkiselev.ksu@gmail.com

Received 16 April 2012; Accepted 6 May 2012

Academic Editors: M. Esseffar, O. Kühn, and X.-B. Wang

Copyright © 2013 Vladimir D. Kiselev et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The values of the heats of solution (2131 solutions) of different liquid solutes in organic and inorganic solvents were obtained from the literature data on the heat of mixing ($\Delta_{\text{mix}}H$) in the wide range of concentrations. The limit values of the heat of solution of a solute ($i$) in a solvent ($j$) ($\Delta_{\text{soln}}H_{ij}$) were calculated from the limit data of the dependence $\Delta_{\text{mix}}H/\chi_i$ versus $\chi_i$ at $\chi_i \to 0$ and the values of that of a solute ($j$) in a solvent ($i$) ($\Delta_{\text{soln}}H_{ji}$) from the limit data of the dependence $\Delta_{\text{mix}}H/\chi_j$ versus $\chi_j$ at $\chi_j \to 0$, respectively.

1. Introduction

At the present, there are a lot of data on the heats of mixing of binary liquid systems [1–5] and considerably less data on the heats of solution from direct calorimetric measurements [6–11]. In two handbooks [1, 2] about 2500 tables of data on the heats of mixing ($\Delta_{\text{mix}}H$) of the different liquid solutes in organic and inorganic solvents have been collected, whence the values of the enthalpies of solution were calculated.

It is generally known that the enthalpy of solution is the enthalpy change associated with the dissolution of a substance in a solvent at constant temperature and pressure, resulting in infinite dilution. This process can mentally be separated on three steps:

$$\Delta_{\text{soln}}H^{A/S} = \Delta_{\text{evap}}H^{A} + \Delta_{\text{hole}}H^{S} + \Delta_{\text{int}}H^{A-S}. \quad (1)$$

Here, $\Delta_{\text{evap}}H^{A}$ is the energy of breaking of all the solute-solute interactions in molecular liquid (A), equal to the enthalpy of evaporation (invariably endothermic process), $\Delta_{\text{hole}}H^{S}$ is the enthalpy of optimal destruction and rearrangement of the solvent-solvent part of interactions (invariably endothermic process), and $\Delta_{\text{int}}H^{A-S}$ is the enthalpy of interaction of the isolated molecule of solute (A) placed in the prepared hole of the solvent (S) (invariably exothermic process). The value of the overall enthalpy change is the sum of the individual enthalpy changes of each of these steps and can be positive (endothermic process) or negative (exothermic process). In the case of ideal solution, there is a complete compensation of breaking and forming energy in (1) with zero value of $\Delta_{\text{soln}}H^{A/S}$. In overwhelming majority of measurements, the values of the heat of solution differ from zero and supply with the additional information for analysis of the nature of these steps [10, 11].

Enthalpy transfer from the gas phase to solution is the enthalpy of solvation ($\Delta_{\text{soln}}H^{A/S}$) and can be calculated as follows:

$$\Delta_{\text{soln}}H^{A/S} = \Delta_{\text{soln}}H^{A/S} - \Delta_{\text{evap}}H^{A} = \Delta_{\text{hole}}H^{S} + \Delta_{\text{int}}H^{A-S}. \quad (2)$$

From (2) follows that the relative change of the enthalpy of solvation ($\delta\Delta_{\text{soln}}H^{A/S}$) of compound (A) in the series of solvents is equal to the difference in the enthalpy of solution ($\delta\Delta_{\text{soln}}\Delta H^{A/S}$).

For all enthalpy cyclic processes, there is the possibility to calculate the unknown values of the enthalpy transfer on the base of relative changes of the enthalpy of solution. As an example, the relative changes of the enthalpy of
solvent. The limit value of the heat of solution (1) in the solvent (2) can be calculated from the curve of the dependence \( \Delta_{\text{mix}}H \) versus \( x_1 \) in the range of \( x_1 \) from near-zero to \((0.3-0.5)\). The value of the derivative \( \delta \Delta_{\text{mix}}H/\delta x_1 \) of the best-fitted function at \( x_1 \rightarrow 0 \) is equal to the heat of solution of the compound (1) in the solvent (2). Similar calculations were performed for the heat of solution of compound (2) in the solvent (1) at \( x_1 \rightarrow 1 \). The same results were obtained from the limit data of the dependence \( \Delta_{\text{mix}}H/x_1 \) versus \( x_1 \) at \( x_1 \rightarrow 0 \) or from the limit data of the dependence \( \Delta_{\text{mix}}H/x_2 \) versus \( x_2 \) at \( x_2 \rightarrow 0 \), respectively. As an example, let us consider here the values of the heats of mixing of methyl alcohol and dimethyl sulfoxide at 25°C (Table 1).

From the data of the first and third columns, the dependence \( \Delta_{\text{mix}}H/x_{\text{DMSO}} \) versus \( x_{\text{DMSO}} \) can be easily calculated, and the value of \( \Delta_{\text{soln}}H \) of DMSO in methyl alcohol follows as \(-0.90 \pm 0.05\) \( \text{kJ mol}^{-1} \). Using similar calculation from the data in the fourth and sixth columns, the value of \( \Delta_{\text{soln}}H \) of methyl alcohol in DMSO follows as \(-1.30 \pm 0.05\) \( \text{kJ mol}^{-1} \). From these results, everyone can conclude that the hydrogen bond methanol-DMSO is stronger than that in methanol-methanol in agreement with experimental data [14]. In these calculations, the more important data of \( \Delta_{\text{mix}}H \) are at the values of \( x_1 \rightarrow 0 \) and \( x_1 \rightarrow 1 \). But as a rule, the lowered heat of mixing is accompanied by the larger error. Therefore, the curvature of the dependence \( \Delta_{\text{mix}}H/x_i \) versus \( x_i \) gives often more correct data than that of single value of \( \Delta_{\text{mix}}H/x_i \) at the small concentration of \( x_i \).

Very sharp curvature of the dependence \( \Delta_{\text{mix}}H/x_i \) versus \( x_i \) is usually observed at \( x_i \rightarrow 0 \) for solution of H-bonded solutes, as alcohols, in inert solvents (alkanes, cycloalkanes, and carbon tetrachloride). For such solutions, the experimental data on the heat of mixing with relatively high concentration of solutes were excluded from consideration. Usually the errors of the heats of solution of alcohols in alkanes were up to \( \pm (1-2) \) \( \text{kJ mol}^{-1} \) and for other solutions up to \( \pm (0.1-0.3) \) \( \text{kJ mol}^{-1} \). This range of errors of calculated heats of solution is in agreement with the precise data of direct calorimetric measurements [6–11]. Some conclusions can be made from the consideration of the obtained data on \( \Delta_{\text{soln}}H \) (Dataset Item 1 (Table)).

From the analysis of the wide experimental data of the heats of solution and solvation of different solutes in the medium of cycloalkanes, very interesting and useful relation was observed [10]. The value of enthalpy of solution \( \Delta_{\text{soln}}H_{A/c-hexane}[\text{kJ mol}^{-1}] \) can be predicted from the highly-reliable (4) [10]:

\[
-\Delta_{\text{soln}}H_{A/c-hexane} = 5.09 + 1.03 \cdot M R_A. \tag{4}
\]

Here, MR\(_A\) is the molecular refractivity \( \text{cm}^3 \text{ mol}^{-1} \) of solute. It means that enthalpy of destruction of the solvent-solvent interactions \( \Delta_{\text{inter}}H^A-S \) are determined only by the ability of c-hexane-c-hexane interactions and by the value of MR\(_A\) of solute. In other words, the relative enthalpy of interaction of c-hexane with different types of solutes will be the same as in c-hexane with c-hexane. With the known experimental data of enthalpy of solution in c-hexane \( \Delta_{\text{soln}}H_{A/c-hexane} \) and calculated value of \( \Delta_{\text{soln}}H_{A/c-hexane} \) (see (4)), everyone can calculate (see (5)) the important parameter, the unknown value of the enthalpy of evaporation of A:

\[
\Delta_{\text{evap}}H_A = \Delta_{\text{soln}}H_{A/c-hexane} - \Delta_{\text{soln}}H_{A/c-hexane}. \tag{5}
\]

The possibility of chloroform (entries 484–538) and perchloroethane (entries 1611–1615) to generate the H-bonds
with the $n$-donor solvents, even with alcohols, follows from the exothermic values of the heat of solution. Very strong interactions of the liquid Lewis acids with the $n$-donor solvents with formation of $n,v$-complexes can be concluded from observed data (entries 1858–1881). Additional conclusions can be done by the reader.

3. Dataset Description

The dataset associated with this Dataset Paper consists of one item which is described as follows.

**Dataset Item 1 (Table).** Enthalpies of solution ($\Delta_{\text{sol}}H$, kJ mol$^{-1}$) of solutes in various solvents (alphabetic order). The calculated limit values of the enthalpies of 2131 solutions were collected. In the first column are indicated the entries' numbers of solutions (Number). In the second column are shown the names of solutes followed by their values of the enthalpies of evaporation in parenthesis from [15]. In the third column, the solvents appeared in an alphabetical order. In the fourth column are collected the calculated values of enthalpies of solution ($\Delta_{\text{sol}}H$, kJ mol$^{-1}$), after slash is given the temperature, °C, and in parenthesis is the number of tabulated data of the heat of mixing ($\Delta_{\text{mix}}H$) from textbook [1] or [2]. As an example, the data of solution of dimethyl sulfoxide in methanol (entry 946 in the table), $-0.9/25$ (319-1), means that $-0.9$ is the enthalpy of solution in kJ mol$^{-1}$, 25 is the temperature of the measurements, °C, and (319-1) is the number (319) of the table of the heat of mixing in the textbook [1].

- **Column 1:** Number
- **Column 2:** Solute
- **Column 3:** Solvent
- **Column 4:** $\Delta_{\text{sol}}H$

4. Concluding Remarks

Analysis of an experimental data on the enthalpy of solution, collected in Dataset Item 1 (Table), helps to estimate the total energy of solute-solvent interactions. These data can be useful for the selection of appropriate solvents for the practical goals in the synthesis and purification and for the theoretical consideration of the constituents of the solution and solvation processes.

**Dataset Availability**

The dataset associated with this Dataset Paper is dedicated to the public domain using the CC0 waiver and is available at http://dx.doi.org/10.7167/2013/823638/dataset.

**Acknowledgments**

This work was supported by the Russian Federal Agency of Education (no. P-2345, GK no. 14.740.11.0377, GK no. OK-1/2010) and the Russian Fond for Basic Researches (Grant no. 12-03-00029).

**References**
